

Replicate Wolter-I X-ray Mirrors

D. E. Engelhaupt
The University of Alabama in Huntsville

R. Rood, S. Fawcett, C. Griffith and R. Khanijow
NASA Marshall Space Flight Center
Huntsville, AL

ABSTRACT

Cylindrical (hyperbolic - parabolic Wolter I) mirrors have been electroformed from nickel over an electroless nickel-phosphorous (NiP) plated aluminum mandrel in support of the NASA AXAF-S x-ray spectrometer program. The electroless nickel was diamond turned and polished to achieve a surface finish of 10 angstroms rms or better. Gold was then plated on the nickel alloy after an electrochemical passivation step. Next a heavy layer of pure nickel was plated one millimeter thick with controlled stress at zero using a commercial PID program to form the actual mirror. This shell was removed from the NiP alloy coated mandrel by cryogenic cooling and contraction of the aluminum to release the mirror. It is required that the gold not adhere well to the NiP but all other plated coatings must exhibit good adherence. Four mirrors were fabricated from two mandrels prepared by this method. The area of each part is 0.7 square meters (7.5 square feet).

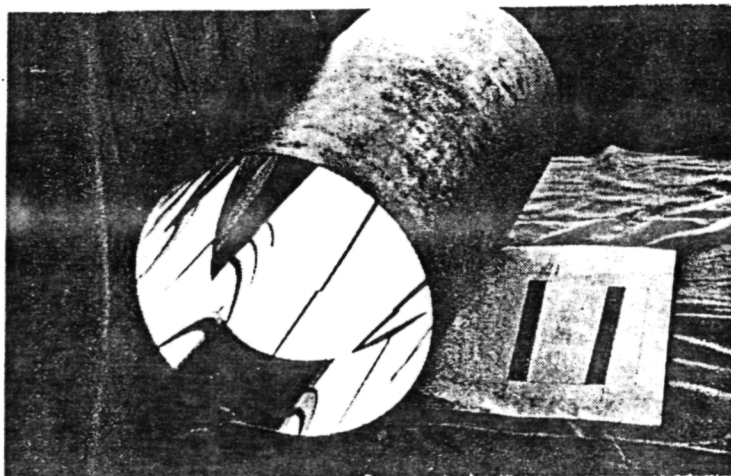


Fig. 1 Electroformed Wolter I grazing incidence mirror
(NIPS-95-05520) REPLICATE WOLTER-I N96-13162
X-RAY MIRRORS (NASA. Marshall
Space Flight Center) 12 p

Unclass

(NASA-TM-111117)

1.0 INTRODUCTION

Fabrication of first surface optical components by coating diamond machined aluminum with electroless nickel and subsequently diamond machining and/or polishing the nickel has been reported with typical final component surfaces achieved about 20 to 50 angstroms rms. The alloy preferred is 11 wt% phosphorous, $\text{Ni}_3(\text{P})$ where the parenthesis denotes an amorphous rather than crystalline deposit. A low stress deposit with sufficient hardness to support an excellent surface finish is achieved at low plating rates by suitable adjustment of the plating parameters. Ref. (1,2,3) Also cylindrical x-ray mirror fabrication by electroforming nickel over an aluminum mandrel coated with electroless nickel and polished similarly has been reported. (4,5)

In order to overcome numerous problems with quality control this task extended beyond the previously reported efforts. Since the flight mirror surface requirement was less than 10 angstroms rms, examination of the stability of the polished $\text{Ni}_3(\text{P})$ surface oxidation was examined by SEM, AUGER and ESCA as well as electrochemical polarization tests to determine the extent of subsequent process degradation on the polished and inspected surface. Also circularity requirements were such that even very low residual internal stress in the electroformed nickel would cause excessive distortion if not controlled in real-time. This required a major effort to achieve the x-ray quality optical components using the first surface as a mandrel for replication.

A commercial electroless nickel process was selected which produced the requisite alloy with no indications of porosity when operated at low pH and high temperature. Replication of the surface was at the gold interface to the nickel - phosphorous requiring a debonding oxide film formation without disturbing the 10 angstrom rms polished surface prior to gold plating. The gold was plated on site from an alkaline non-cyanide electrolyte for three shells and from an off site contracted vacuum evaporation system for the fourth shell. This was followed by a 1.0 millimeter thick nickel electroformed shell, with real-time control of the internal stress, which became the actual

optical component. Separation of all four shells was successful by using liquid nitrogen to cool the composite Al/Ni₃(P)/Ni_xP_yO_z/Au/Ni assembly until the mandrel shrank sufficiently to release at the gold/Ni_xP_yO_z layer.

2.0 MANDREL MATERIAL SELECTION

The typical aluminum alloy selected for diamond turned optics is 6061 due to good diamond turning response. The material is typically purchased as wrought remelt alloy and contains a large amount of inclusion impurities. No large item first melt pure aluminum addition 6061 is known to be available in the U.S.

The aluminum mandrel alloy selected for the AXAF-S mirror program was 2024 since it has a higher copper content which promotes less porosity in the plated coating and also since it can be forged. The lower porosity is believed to be due to lower inclusions of iron and also the dissolution displacement of copper on the included iron particles during preparation for plating which in turn permits better coverage of inclusions by the nickel alloy plating process.

Since the parts are very large optics (0.33 meters diameter by 0.71 meters long) it was necessary to forge the mandrel blank. The alloy was received in the "F" condition after forging. Since 2024 is not a common forging alloy precautions were taken to assure that no residual stress would be in the material at the time of diamond turning noting that it is not necessary or even desirable to achieve the highest hardness and strength for this application. Therefore the 2024 aluminum material was taken to T-6 and then overaged to relax all internal stress from previous steps at the expense of hardness and tensile strength reduction.

2.1 Mandrel preparation procedures

- 1) 21 Hours at 850 deg. F.
- 2) Forge until temperature drops to 700-740 deg. F.
- 3) Reheat at 850 deg. F. for 3 hours.
- 4) Second swage with temperature above 700 deg. F.
- 5) Air cool and ship to MSFC.
- 6) Solution heat treat at 920 deg. F per MIL-H-6088F.
- 7) Boiling water "uphill" quench.

- 8) Precipitation harden 18 hours at 375 deg. F.
- 9) Stress relief after machining 1 hour maximum at 500 deg. F.
- 10) Reverse quench, LN₂ stabilize, steam blast.
- 11) Final machine.
- 12) Post machine stabilize thermal cycle +200 deg. F to -100 deg. F then to Room Temperature.
- 13) Diamond machine allowing for nickel - phosphorous plate.

2.2 Electroless nickel plating

The next step was electroless NiP plating. The plating processes were selected on the basis that no cyanide or hydrofluoric acid would be used. The Ni₃(P) plating process used a citric acid cleaner, HNO₃ deoxidizer and zincate cycle similar to most other processes but then an electrolytic nickel strike from a glycolic acid based solution was used to achieve adherence and coverage of any inclusion sites. The process produced a very low plating rate at pH 4.2 which was also due in part to the addition of sub-ppm stabilizer additives which in turn promoted a deposit with outstanding quality performance. This was evidenced by the complete absence of micro-porosity over the entire 0.7 meter² (7.5 ft. sq.) surface of each of the two mandrels processed. The Ni₃(P) was heat treated at 160 deg. C (320 deg. F) for 4 hours to promote additional adhesion without crystallization to Ni₃P.

Next the mandrel was sent to the diamond turning and polishing lab where the surface was produced to less than 10 angstroms rms by re-turning the Ni₃(P) with a single crystal diamond and polishing with aluminum oxide and either diamond or silica gel.⁽⁶⁾

2.3 Electroless nickel passivation

In order to gain better control of the adhesion, or more appropriately minimized adhesion of the gold, a more fundamental understanding of the nature and behavior of oxide films on high phosphorous nickel alloys was undertaken using potentiostatic methods along with SEM, AUGER, ESCA and AFM.

The formation of oxide films on metals proceeds differently depending upon many conditions. It must be considered that the oxide film is a mixture of metal and oxygen and that unless supplied by another source the metal is nominally diffused from the metal surface by a corrosion process. This in turn may well degrade the 10 angstrom polished surface of interest for the replication process. First, spontaneous oxide formation in humid air or in water occurs for nickel.

The pH, time and temperature determine the extent of oxidation with a maximum at about 160 - 170 deg. F in pH 7.0 water or high humidity. The film formed will generally increase in oxygen toward the surface. The oxide film is semi-conductive with local sites of higher conductance as a result of film formation defects. The "defect" sites have been studied for many systems and agreement is that increased ionic and electron mobility occurs when the atomic arrangement surrounding atoms of reduced coordination is not of the same stoichiometry as the bulk film.

This generally causes patches of non-conductive oxides in a field of ambipolar conductive points. Thus the stoichiometry and thickness for a spontaneous film are not well controlled. Discolored gold deposits may occur on this type surface and are most likely dendritic spires of gold occurring at the defect sites. Adherence will occur at these sites and the gold will not plate smoothly across the non-conductive patches due to localized high current density at the defect sites which causes patchy microscopic diffusion limited deposits which are rough.

The need is therefore to achieve a very thin and uniformly conductive oxide (semi-conductive) film with no defect sites or with such a multitude of defect sites that the conduction appears to be continuous. The initial passivation process studied consisted of a brief immersion of about two seconds in 2% NaOH followed by 5% K_2CrO_3 without current for five seconds. After forming a very thin oxide film and upon immersion in a hexavalent chromium solution a semi-conductive film (perhaps II-VI in nature) is formed and subsequently permits uniform electrodeposition of gold with the required low adhesion for subsequent release.

Since hexavalent chromium is both toxic and a substantial contaminant for other plating operations it was desirable to eliminate this step. The short immersion times found suitable on the small samples was not achievable on the actual AXAF-S hardware due to the size and weight requiring a slow hoist.

An anodically formed film with an included cation was believed to be most appropriate. The substitution of nickel for the chromium would be most desirable. Thus alkaline processes containing nickel complexes were investigated. When the nickel-phosphorous alloy is made anodic in an alkaline nickel tartrate or other nickel ligand forming solution, a conductive nickel rich oxide surface rather than a non-uniform nickel oxide, phosphorous surface is formed. For pure nickel in an alkaline solution the progression of anodically induced oxide formation is in the order; $\text{Ni}(\text{OH})_2$, Ni_3O_4 , Ni_2O_3 and NiO_2 . By adding a complexing agent such as tartrate, the progression of the oxide formation is reduced to two observable steps (i.e., slow) and a more negative and stable reduction of the oxide is observed by cyclic voltammetry. See figures 2,3.

Nickel-Phosphorous alloy samples made anodic in an alkaline nickel tartrate solution have been found to form a uniformly conductive Ni/P/oxide surface.

This surface formation can be controlled potentiometrically to form a film less than 10 angstroms thick containing nickel, phosphorous and oxygen which permits a readily deposited and subsequently removable gold deposit. The presence of carbon was persistent in the outermost film but appeared even in films formed from reagent grade sodium hydroxide indicating that the carbon was adsorbed from the air or from carbonates in the solution.

2.4 Gold to Nickel-Phosphorous Adhesion

Initial tests plating from an acid gold cyanide solution onto nickel-phosphorous alloy of 6% phosphorous were inconclusive. By electrolyzing the nickel phosphorous sample cathodically in an alkaline cleaner and then passivating in a five gram/liter potassium dichromate solution it was possible to achieve various levels of adhesion.

Using cathodic treatment followed by simple immersion in the chromate solution no release of the gold was observed. By making the sample cathodic in the cleaner for 30 seconds and then anodic in the chromate solution, complete passivation occurred and the highly stressed acid gold cyanide process failed to produce an adherent deposit causing blistering and peeling of the gold.

Reduction of the thin oxide film must not occur due to the gold deposition process. The acid cyanide gold-cobalt process first employed plates with low efficiency with the evolution of hydrogen concurrent which reduces the nickel oxide and possibly complexes nickel with cyanide. This results in adhesion of the gold to the substrate even with an oxide film initially present.

Polished one inch diameter flat samples of 11 wt% phosphorous NiP deposit were plated in an alkaline gold sulfite process. This process will not readily reduce the oxide film and permits deposition with low adherence on the passivated NiP surface permitting separation of the shell later. The Faradaic efficiency of the gold plating must be near 100% which requires careful control of the pH to a somewhat high value between 10 and 10.5. The initial passivation consisted of simple immersion in 5 grams/liter NaOH for 30 seconds and 5 grams/liter K_2CrO_3 for 5 seconds although the mirror could not be handled this quickly.

A smooth gold deposit was obtained on the dichromate passivated surface which readily lifted with cellophane tape. Electrodeposition of nickel onto these flat samples resulted in excellent repeatable separation at the gold/oxide layer.

Next tests were conducted to determine proper conditions for anodic passivation. Low anodic current from 2 to 4 mA/cm² from 5 to 10 seconds resulted in film formation which could be gold plated and subsequently the gold could be lifted with cellophane tape. When samples were prepared using 5 mA/cm² for 10 seconds anodic passivation in 5 gm/liter NaOH, the gold was not uniformly deposited and required replating. Additional tests were performed using electroless nickel on con-

cal aluminum samples. Both quantitative tensile testing with a load frame and qualitative tape pull release of the gold was readily achieved on samples by using the alkaline nickel tartrate solution. However when the much larger mandrels were prepared it was found that this relationship was not linear. A potential monitor was set up using a pH meter in the potential mode connected to a recorder to monitor the formation of the oxide film on the actual mandrel in real-time. This allowed the oxide film growth to be observed to determine the extent of the film formation. See figure 4.

2.5 Gold plating process selected

The passivated $\text{Ni}_3(\text{P})$ surface was plated using an alkaline sulfite gold process at a pH of 10.5. The potentiometric passivation in 0.1 M nickel and sulfate buffered pH 11.0 0.1 M Rochelle salt (sodium potassium tartrate) was employed. A smooth gold deposit was obtained which readily lifted from the electroless Ni in most cases but a very light haze was observed when observed under bright light. Also on occasion during the testing of coupons the deposit was very dark and so poorly adherent that it would peel spontaneously. By reducing the natural oxide cathodically in 0.2 N sodium hydroxide at 20 mA/cm^2 for 5 minutes and then forming the desired film anodically as previously described, better control was achieved.

Samples of the gold electroplated and separated from the passivated electroless nickel were subjected to ESCA and AUGER analysis for chemical analysis to determine if the oxide film was separated from the NiP and remained with the part.

The analysis showed some oxide and even some traces of the nickel plating process may have been present in the interface. This was removed by immersion in 25 vol% H_2O_2 overnight.

Vacuum deposition of pure gold on a clean Ni-11 wt% P substrate after argon sputtering (no electrochemical passivation) produced similar results in that overall very low adherence was achieved.

Locally adherent areas of vacuum evaporated gold were difficult to release with differential thermal expansion from one of the smaller test shells produced with this process. This resulted in small patches of gold not releasing from the mandrel on the test piece. Fortunately when the second large mandrel was coated with gold in a vacuum evaporation system the separation of the last electroformed nickel shell was readily performed with no such anomalous attached spots. This is possibly due to the relatively long time period the part remained in air prior to plating which would extend the surface passivation.

2.6 Nickel electroforming

The use of an active sensor to monitor the stress induced in the sulfamate process electroformed nickel shell permitted an on-line method of controlling the stress in real-time. The current density first had to be as uniform as possible. This was mapped using a second monitor and changes in the configuration of the plating equipment were implemented to provide a uniform field and subsequently uniform current density and thickness. The thickness of the part was later measured by CMM to be within 0.0025 centimeter variance over the length of the part. Optical measurements demonstrated that the circularity and optical figure were excellent when proper control was implemented but without this control the quality was not adequate for x-ray applications. See figure 5.

2.7 Final Cryogenic Separation of Shell:

After electroforming the nickel shell the part was returned to the diamond turning center and the shell was trimmed to exact length on the mandrel. The part was then cleaned for separation. The mandrel was hollow and about two inches thick permitting the LN₂ to be pumped into the center thus cooling the part from the inside. Care was taken not to locally heat any part of the shell to avoid thermal difference stress. Thermocouples were used on the outside and when the temperature dropped sufficiently an audible click was heard and the shell was free. This occurred slightly above freezing water temperature at the outside of the shell. The shell was lifted carefully straight up to avoid scratching the surface. The focus was better at

the longer x-ray wavelengths primarily due to scattering of the x-rays however by the fourth mirror very near flight quality results were achieved.⁽⁶⁾

3.0 REFERENCES

- 1) "Observations on Polishing Electroless Nickel Plated Surfaces"

R. Parks and C. Evans, April 1991 ASPE Spring Topical Meeting, Tucson, AZ
- 2) "Electroless Nickel Plating for Enhanced Gold Coating:
A Lesson in Bimetallics"

Steven Scott, April 1991 ASPE Spring Topical Meeting, Tucson, AZ
- 3) "Influence of Phosphorous Content and Heat Treatment on the Machinability of Electroless Nickel Deposits", Ibid

C. Syn, et al, Lawrence Livermore National Laboratories
- 4) "Results of X-Ray Measurements on Electroformed Mirror Shells for the XMM Project"

O. Citterio, P. Conconi, F. Massoleni, et al, Interim report for European Space Agency for X-Ray Astronomy Jet-X X-Ray Telescope, ESA Contract No. 9685/91/NL/MS.
- 5) "Imaging Characteristics of the Development Model of the JET-X X-ray Telescope"

O. Citterio, P. Conconi, F. Mazzoleni, et al, SPIE Vol. 1546 Multilayer and Grazing Incidence X-Ray/EUV Optics (1991)
- 6) "Wolter I X-ray Optics Produced by Diamond Turning and Replication" S. Fawcett, et al of NASA MSFC, Huntsville, AL. SPIE International Symposium on Optics, Imaging and Instrumentation, 24-29 July 1994 in San Diego, CA.

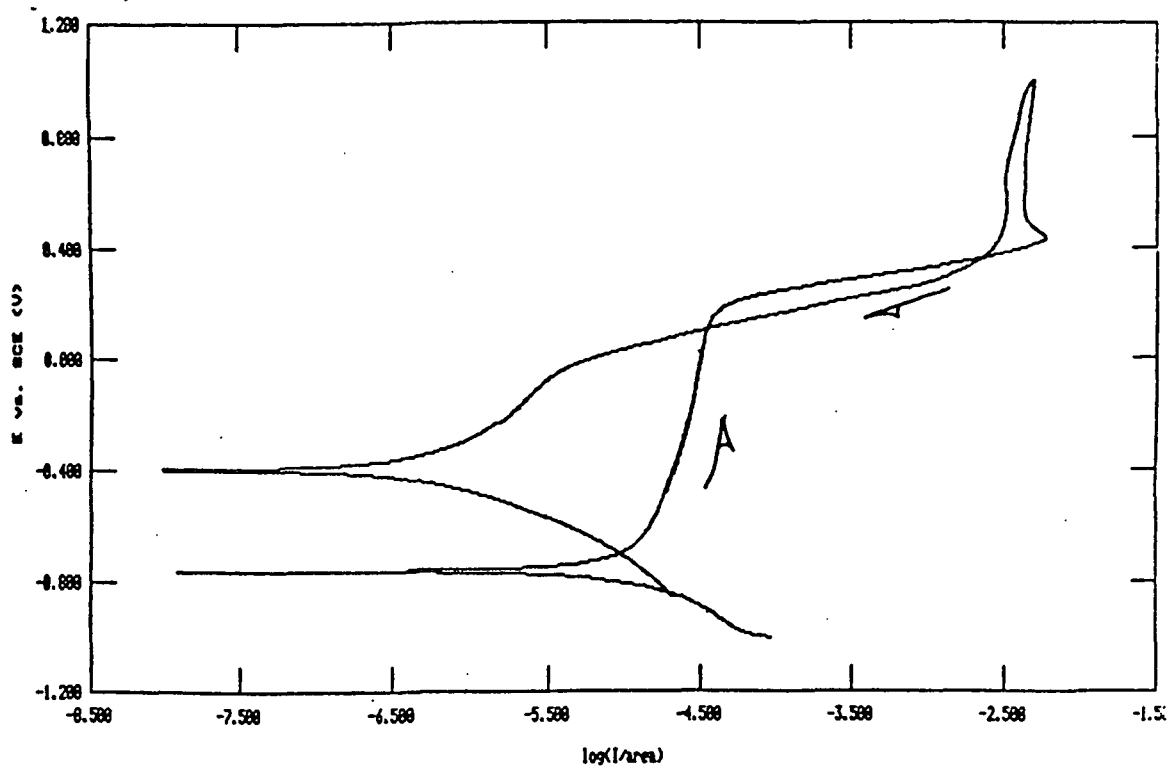


Figure (2)

0.1N NaOH
0.1M Rochelle Salt
0.1M Ni^{++}

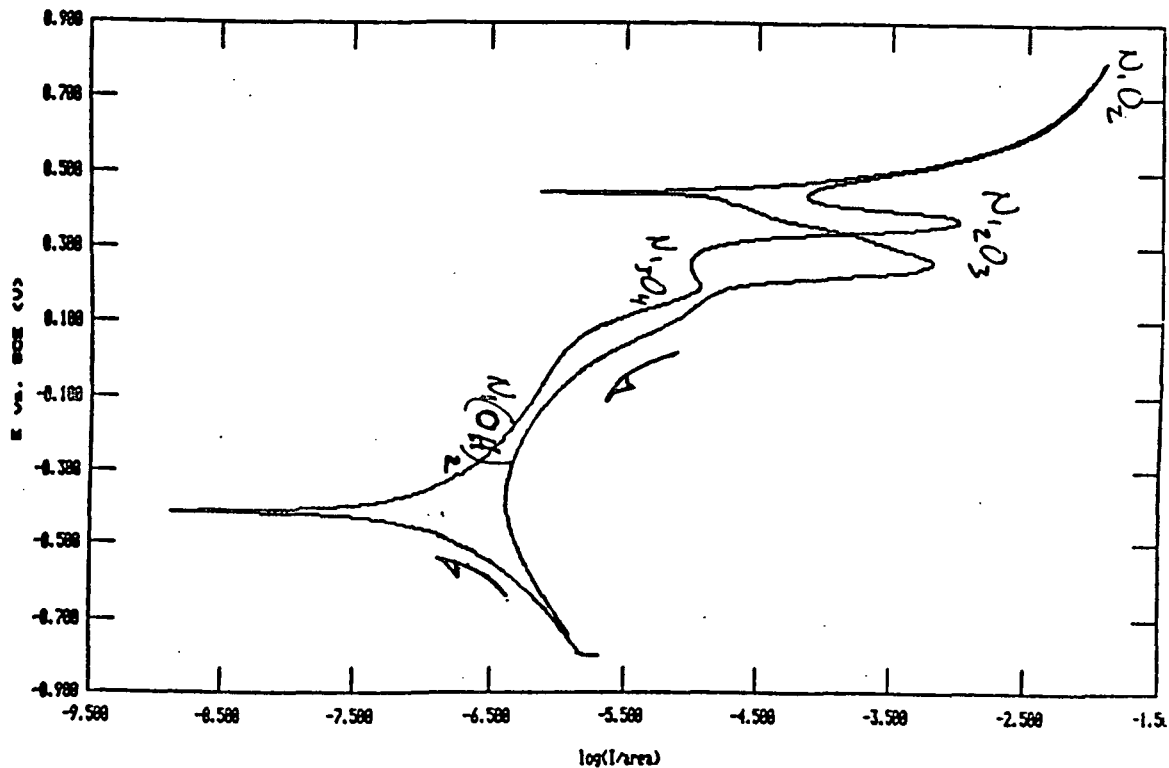


Figure (3)

0.1M NaOH R.T.

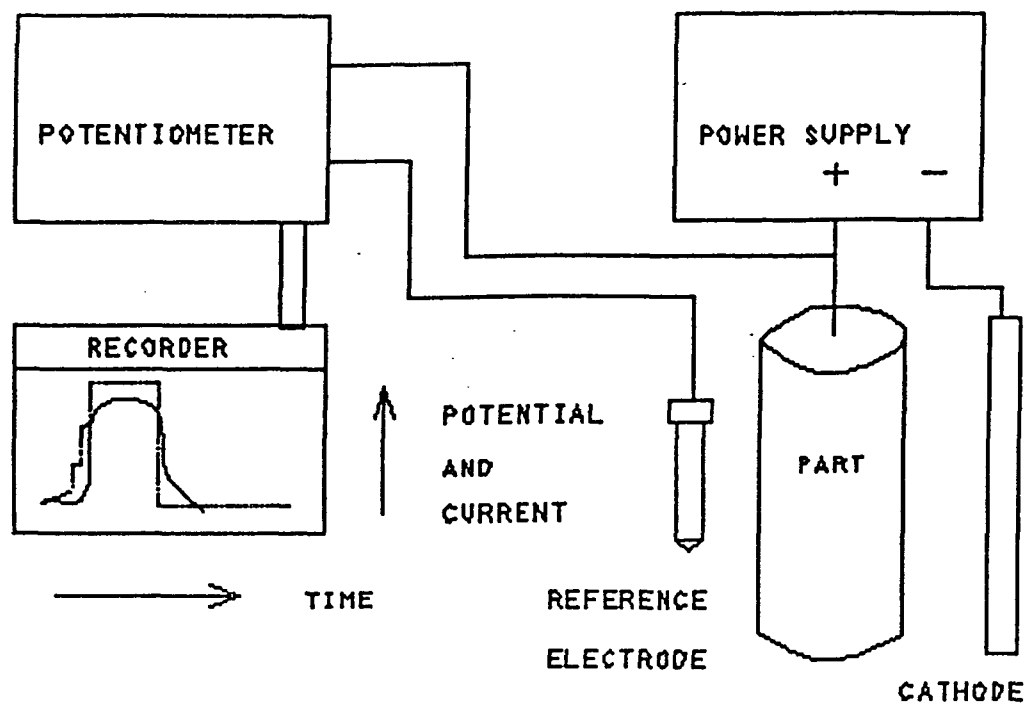


Figure 4. Schematic of monitor used to control passivation

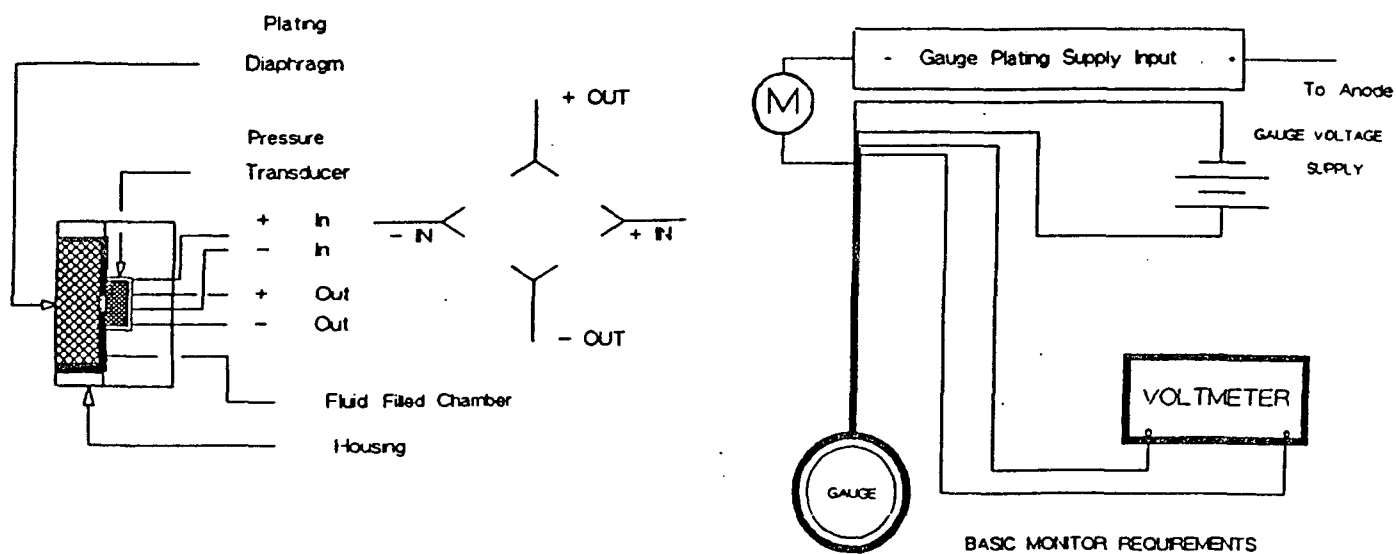


Figure 5. Schematic of monitor for control of plating stress